Functionalising graphene: It's got to be done, so let's do it

Everyone agrees that graphene holds massive promise. Possessing a unique portfolio of desirable properties, including excellent conductivity, mechanical strength, gas barrier, thermal and biocompatibility, graphene is an intriguing material.

The physical nature of the graphene platelets is important: Factors such as the uniformity, platelet size and the number of graphene platelets in a stack have a fundamental effect on the physical and chemical properties of the graphene, which in turn affects the efficacy of the graphene in its intended use.

In addition to the physical properties, the next factor to be considered is what chemical functionality is necessary for the graphene to work in the desired application. An intrinsic feature of pristine graphene platelets is their lack of chemical functionality; however, in order to use graphene in a commercial viable application, functionality is essential so that the material can be processed using conventional manufacturing techniques such as injection moulding, roll to roll coating or printing. Functionalisation brings:

- Controlled increase in solubility for processing in solvents/water and polymers; there are a limited number of solvents and materials into which graphene will disperse without the need for additives such as surfactants.

- Controlled compatibility with the surface-surrounding matrix (e.g. polymers); pristine graphene platelets can be considered to be chemically inert to most standard chemistries. This means when mixed into a coating or binder there will be little to no strong chemical interaction between the graphene and the matrix.

One of the obstacles to realising graphene's potential is the need to functionalise with the minimum disruption to the intrinsic properties. This can be achieved by the chemical modification of graphene to impart the desired chemical properties to the platelets.

Through chemical modification it is possible to alter both the solubility sphere and the chemical compatibility of the graphene. This mitigates or reduces the need for surfactants and enables dispersion in a wider range of solvents or materials. In addition it directly affects the efficiency with which graphene can interact and reinforce a chemical matrix.

The requirement for chemically modified materials is not new and the benefits of successful modification are profound. This is clearly demonstrated in the case of Glass Fibre or Carbon Fibre reinforced composites. Early attempts to prepare composite materials from these fibres with an epoxy matrix resulted in inferior physical attributes to those anticipated. It was only with the development of chemical modifications, such as silanes and sizing agents which alter the chemical properties of the fibre increasing wetting and chemical bonding, that the true potential of these reinforcement agents was delivered. These chemical treatments have enabled the development of the light weight composite components we see today, which are used in major applications such as aerospace, transportation and renewable energy.

The use of functional graphene is therefore a fundamental part of new product design and should be factored into the plan for the product in the earliest stages of development.

One of the key features of graphene is the excellent overall chemical stability of the multi-ring system. So any reactant has to be intrinsically potent while at the same time being easy to incorporate into an overall process and, ideally, easy to switch on at will.

OAS believes that the capabilities of their Onto™ surface modification platform fit very well into those key requirements for a material modification:

- It uses a highly reactive carbene chemistry already proven with many "inert" systems such as polyethylene;
- The carbene precursors are stable and processible via standard solution chemistry in solvents and/or water;
- The carbenes can be switched on via heat or UV light; and
- The carbenes can be integrated with a wide range of other functionalities that can be exploited in the target application; small-molecule single functional groups for specific interactions, "solubilizing" chains for general solubility improvements, multi-functional polymers for strong (entangled) adhesion to surfaces or polymer matrices.

Carbene intermediates have a unique reaction profile which includes the insertion in to atom-Hydrogen bonds as well as the addition to sp2 and sp hybridised carbon-carbon bonds (Figure 1). This reaction profile is unique to carbenes as it allows direct carbon-carbon bond formation with non-activated systems.

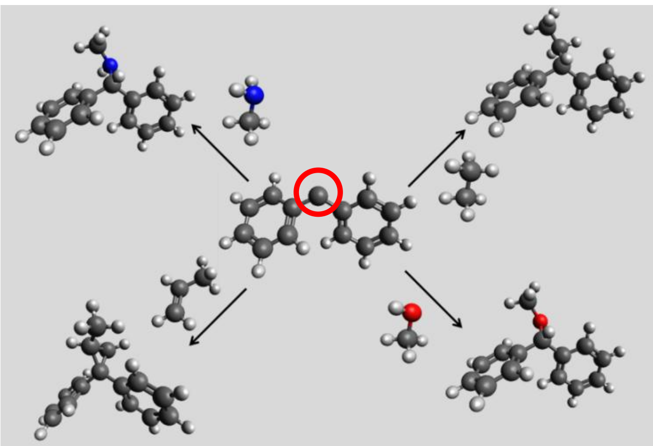

Figure 1 *Overview of key carbene reactions when applied to surface modification of organic materials. Top Left: Insertion into N-H bond; Top Right: Insertion into C-H bond; Bottom Right: Insertion into C-O bond; Bottom Left: Addition to C=C bond. The carbene is circled in red.*

This broad reaction profile makes carbene reactive intermediates ideally suited for surface modification of both organic and inorganic materials as virtually all organic materials have some C-H or C=C bonding. This reactivity has been proven to be accurate with successful modification demonstrated on a large variety of "inert" materials such as HDPE, PEEK, PEN, carbon black Diamond DLC (Diamond-like-carbon), CNT, carbon fibres, C_{60}.

Onto™ treatments can be prepared with specific functionality so that they are tailored for a specific application. For example the wetting/dispersibility of a material can be modified by the introduction of long non-polar side groups which will increase the hydrophobic nature of the material thus increasing its dispersibility or affinity for organic solvents. The introduction of a polar side group chemistry will render the material hydrophilic thus increasing the dispersibility of the material in polar materials such as water and alcohols. Adhesion properties and chemical compatibility can be similarly altered by selecting a side group functionality to match that of the adhesive or coating. Thus it is possible to improve significantly the chemical interactions between surface and coating leading to improved adhesion or bonding.

This approach is analogous to that used on glass fibre sizing with silane adhesion promoters with the added advantage in that unlike silane treatments the Onto™ process can be applied to both inert organic and inorganic materials.

OAS is now investigating the use of its Onto™ technology to modify graphene chemically for multiple applications. The ability to modify both the dispersibility/affinity of the graphene for a solvent or coating, and to improve the chemical interaction and adhesion of the graphene within a coating, is a powerful tool in the production of commercially relevant graphene-based applications and products.

OAS is currently looking into the applications and requirements for chemically modified graphene in areas such as composites and electronics. In addition to the internal development for graphene modification, OAS is actively seeking partners for co-development of commercial applications with both graphene suppliers/manufactures as well as end users, converters and specifiers.

We welcome any enquiries regarding the surface functionalisation of graphene. Interested parties should contact OAS:

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